On the Nature of Foam. VIII. Foam Phenomena of the System Saponin—*i*-Amyl Alcohol—Water.

By Siro MITUI and Tunetaka SASAKI.

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The problems of foam are frequently taken up from the practical stand point, chiefly concerning the determination of the condition of foam formation or destruction. Foam phenomena can also be treated with theoretical interests either because of their being used as a means for observing surface properties of a solution in which they are produced, or of many valuable suggestions obtained by seeking for analogies among foam and other types of dispersion systems, viz., suspension and emulsion.

Now, let us briefly describe the studies on these lines. Ramsden[1] observed that bubbles of a mixed aqueous solution containing two solutes sometimes behave just like those of solutions containing either one of the two components, and this he explained by the selective adsorption at the surface of bubble film. Thus, he concluded in the case of mixed aqueous solutions of two solutes, for example, bile salt–saponin, saponin –egg albumin, and egg albumin–carmin, that the former solutes are adsorbed at the surface of solution with the exclusion of the latter. Similar observations were made by Bartsch.[2] Foam of aqueous *i*-amyl alcohol solution is stabilized by the addition of relatively large amounts of glycol or glycerin, but very small amount are sufficient in the case of the addition of saponin, albumin, or gelatin. The former solutes are relatively weakly adsorbed than the latter, and their effects on foam stabilization do not become appreciable unless by the addition of large amounts. The same observation was made upon *i*-amyl alcohol–ethyl alcohol–water system. Bartsch,[2] by a number of suggestive experiments, further showed analogies between foam and lyosol as the dispersion systems. According to his idea there are two type of foam, lyophilic and lyophobic, just as in the case of lyosol. The former is produced by shaking a lyophilic colloidal solusion such as an aqueous solution of saponin or soap, while the latter is the foam, for instance, of an aqueous solution of surface active substances such as fatty acids or alcohols. Various resemblances in behaviours between foam and sol were indicated experimentally, mainly concerning the stability of the systems. Ostwald[3] measured the life of bubble produced in a mixed aqueous solution of dye and ethyl alcohol, and concluded that the chage in degree of dispersion of the solute affects the life of bubble. Rehbinder[4] found the relation between the rigidity of foam film and the type of bubble life concentration curve. In the case of less rigid film, the curve shows sharp maximum

(1) Ramsden, *Z. physik. Chem.*, **47**(1904), 336.
(2) Bartsch, *Kolloid-Z.*, **20**(1925), 1.
(3) Ostwald and Quast, *Kolloid-Z.*, **48**(1929), 156.
(4) Rehbinder and Wenström, *Kolloid-Z.*, **53**(1930), 145.

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in life at a certain concentration and decreases to zero at higher or lower concentration of the solute, while, as the bubble film becomes more rigid, the limiting life at concentrated solution grows up from zero to a finite and larger value and the maximum of the curve becomes less marked, and finally disappears.

As for the properties characterizing foam, we can cite its rigidity,[5] compressibility[6], liquid or gas contents[7], and degree of dispersion[6], of which however detailed studies are not available. One of the present authors also made experiments on foam formation of saponin—ethyl alcohol—water system, and attempted some explanations from the same point of view[8]. To secure more precise informations, foam phenomena of saponin—*i*-amyl alcohol—water system (SAW-system) were studied, and the results were reported in the present paper.

Experiment. We measured the height and life of foam produced in an aqueous solution of SAW-system, where the concentration of saponin was kept constant to 0.0092 g. per litre, while that of *i*-amyl alcohol varied from zero to saturation. Foam is produced by a kind of shaking machine reported in the preceding paper[8] and in such a manner as discribed in the following; 10 c.c. of the solution for measurement is introduced in a well stoppered test tube (1.5 cm. in diameter and 15 cm. in length) and is shaken 50 times for 10 minutes with an amplitude of 12 cm. Height of foam (H), immediately after the stop of shaking, and its life (L), the time required for perfect disintegration of foam, are recorded, from which H—conc. and L—conc. curves are obtained. The results were shown in Table 1, Figs. 1 and 2. We further calculated the reciprocal number of coagulation velocity ($1/V$), namely the stability (S), of foam as a dispersion system.

$$S = \frac{1}{V} = \frac{L}{H}$$

The values were shown in the 5th column of Table 1, and S—conc. curve was depicted in Fig. 3.

The values of L, H, S. for binary mixture of *i*-amyl alcohol and water (AW-system) were measured at the same time for reference, and were also shown in Figs. 1, 2 and 3.

Discussion. (1) First of all, we notice in these figures the pronounced increase in values of S and L at very dilute solution of SAW-system; that is, these begin to increase already at the concentration of $10^{-4.5}$~10^{-5} mol. per liter (called C_0 concentration for convenience) and amount to very large value at the concentration of about $10^{-3.5}$ mol. per litre of *i*-amyl alcohol. These phenomena are striking, as one thousandths or one ten thousandths of *i*-amyl alcohol concentration is sufficient for remarkable foam formation compared with the case of AW-system which, owing to the absence of minute quantities of saponin, posseses a corresponding C_0-value of about $10^{-1.2}$ mol. per litre.

(5) Derjaguin and Obuchov, *Kolloid-Z.*, **68**(1934), 243.
(6) Derjaguin, *Kolloid-Z.*, **64**(1933), 1.
(7) Siehr, *Kolloid-Z.*, **77**(1936), 27.
(8) Sasaki, this Bulletin, **15**(1940), 449.

Table 1.

Conc. of Saponin (g./l.)	Conc. of *i*-Amyl Alc. (mol./l.)	H (cm.)	L (sec.)	S (L/H)
0	0	0	0	—
0	3.217×10^{-5}	0	0	—
0	1.082×10^{-4}	0.4	1	2.5
0	3.637×10^{-4}	1.3	5	3.84
0	1.223×10^{-3}	1.6	11	1.84
0	1.383×10^{-2}	2.6	19	7.31
0	4.649×10^{-2}	2.7	63	23
0	9.298×10^{-2}	2.8	426	152
0	1.444×10^{-1}	2.4	780	325
0	1.563×10^{-1}	1.9	>900	>473
0	1.701×10^{-1}	1.9	>900	>473
0	1.796×10^{-1}	1.3	>900	>473
0	2.148×10^{-1}	0.7	625	>473
0	2.391×10^{-1}	0	0	—
0	3.202×10^{-1}*	0	0	—
0.0092	0	0.7	ca 62	88.6
0.0092	2.225×10^{-8}	1.0	64	64.0
0.0092	7.483×10^{-8}	0.8	45	56.3
0.0092	2.516×10^{-7}	0.9	41	45.5
0.0092	8.461×10^{-7}	0.7	32	45.7
0.0092	2.845×10^{-6}	0.7	58	82.8
0.0092	9.566×10^{-6}	0.7	68	97.1
0.0092	3.217×10^{-5}	0.9	160	155
0.0092	1.082×10^{-4}	1.6	433	>155
0.0092	3.637×10^{-4}	2.5	>600	>155
0.0092	1.223×10^{-3}	3.1	>600	>155
0.0092	4.112×10^{-3}	3.4	>600	>155
0.0092	1.383×10^{-2}	3.9	>600	>155
0.0092	4.649×10^{-2}	3.5	>600	>155
0.0092	8.941×10^{-2}	3.2	>600	>155
0.0092	1.438×10^{-1}	2.4	>600	>155
0.0092	1.563×10^{-1}	2.4	>600	>155
0.0092	1.622×10^{-1}	2.0	45 min.	>155
0.0092	1.923×10^{-1}	0.8	>600	>155
0.0092	2.090×10^{-1}	0.6	27 min.	>155
0.0092	2.393×10^{-1}	0	0	—
0.0092	3.202×10^{-1}*	0	0	—

* Indicates saturate solution.

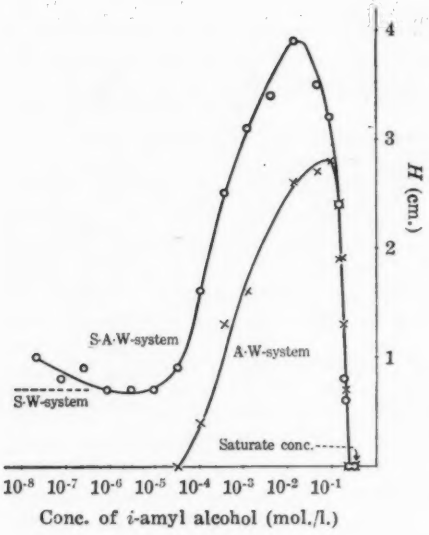

Fig. 1.

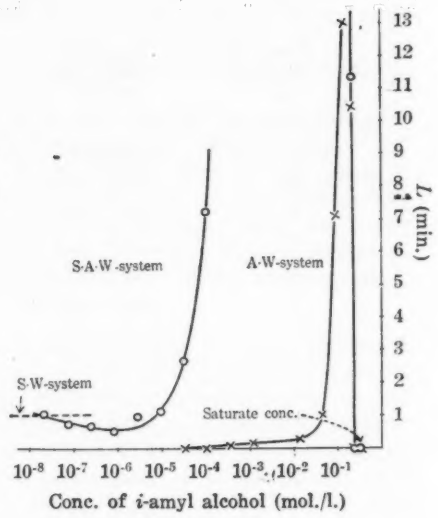

Fig. 2.

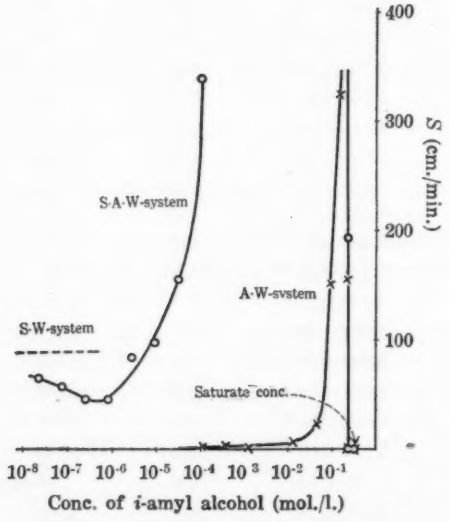

Fig. 3.

When we further compare C_0-value of SAW-system with that of saponin—ethyl alcohol— water system, both of the same saponin concentration (about $10^{-2.8}$ mol. per litre), we recognize that a rule similar to Traube's also holds for C_0-value.

As for the explanation of the increase in amounts of foam formation near the concentration of C_0, we take account of the foam stabilizing action of saponin and the foam producing action of *i*-amyl alcohol, as considered from the relative magnitudes of H to L of SW- and AW-system respectively. In SAW-system near C_0, these two properties affect each other and favour the condition of good foam formation as mentioned in the former report[8]. According to this idea, *i*-amyl alcohol here acts as a dispersing agent.

It is interesting to compare the action of alcohols on systems of various types of dispersion. In oil—water emulsions, the addition of alcohol —called sometimes an introfier[9]—reduces interfacial tension resulting high dispersion, while in suspensions, namely solid in liquid system, alcohol causes dehydration and coagulation rendering the system unstable. Foam system resembles emulsion rather than suspension from such a point of view. This can be understood when we compare the rigidity or hardness of the interfacial films and the special conditions, coming therefrom, in these three systems of different dispersion types. In the case of suspension the effect of alcohol is mainly confined to its influence upon the stability of the dispersion system already formed, while in the case of emulsion and foam where the interfaces are easily deformable, it frequently happens that we must in addition take account of the effect of alcohol on the degree of dispersion during the formation of the system.

Concerning the stabilizing action, saponin behaves similarly in all three systems of different dispersion types. It is evident in Fig. 3, that in the region of optimum concentration, stability of SAW-system is far larger than expected from the sum of the stability of each component. This is perhaps due to the specific properties of mixed adsorption film described later.

(2) When we examine L—conc. or H—conc. curve of SAW-system for wide range of *i*-amyl alcohol concentration, it may be easily noticed that at the dilute concentration, these curved run closely to those of SW-system, while near the saturation concentration, curves coincide with those of AW-system. In the region of intermediate concentration, the curves neither belong to SW- nor AW-system, and the foam formation is proper to the ternary system itself.

Being regarded as one of the measures of surface properties, the foam phenomena as well as the surface tension tell us the behaviour of liquid surface or frequently more sensitively. It is appearent from Figs. 1, 2, and 3 that the properties of SAW-system below C_0-concentration are characteristic of saponin solute as far as the foam phenomena are concerned. The surface of the solution behaves as if it is a simple solution—here the liquid surface is considered separately as a kind of solution phase —although the bulk phase contains two solutes. Surface activity of *i*-amyl alcohol grows effective at concentrations exceeding C_0 which at least indicates the formation of a mixed adsorption layer consisting of saponin and *i*-amyl alcohol. In the latter case, therefore, both the surface and bulk are mixed solutions. In SAW-system of very high *i*-amyl alcohol

(9) Holms, "Laboratory Manual of Colloid Chemistry," *3rd Ed.*, 167, New York (1932).

concentration, the foam properties solely coincide with that of AW-system, probably as the result of saturation of adsorption layer with *i*-amyl alcohol, with the exclusion of saponin. In this region, the foam formation of the system decreases to zero shortly before the saturation of *i*-amyl alcohol as it is so with AW-system. *i*-Amyl alcohol often acts as an antifoam under these conditions.

In the above discussion, we attempted to make use of the foam phenomena for the detection of the behaviour of liquid surface, which of course merely suggests one of the possible interpretations of the phenomena observed. These ideas, for instance, were adopted by Ramsden[1] as has been described and also, more recently, by Dunken, Fredenhangen and Wolf[10] who made experiments on the interfacial tension between mercury and *i*-amyl alcohol from the same point of view. The latter authors as well as Ostwald[3] further sought in the bulk of solution for the explanation for changes in surface properties, and pointed out as a factor the alteration in degree of dispersion of the solute. We did not refer so far in the present experiment, but a few properties related to surface and bulk of the solution were measured for further references.

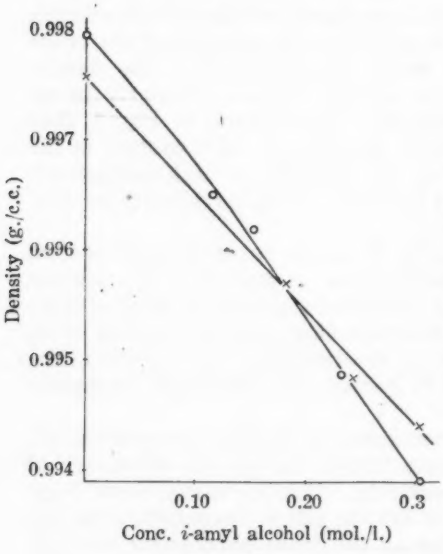

Fig. 4.

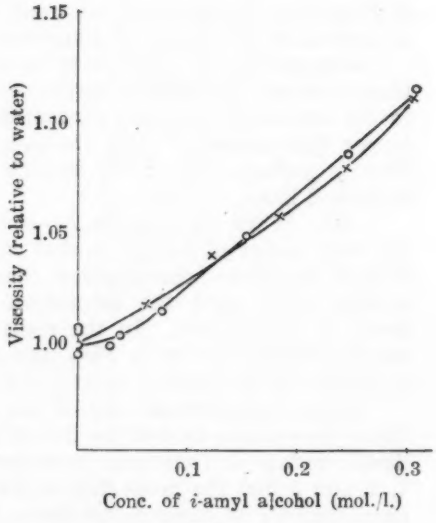

Fig. 5.

Figs. 4 and 5 represent density— and viscosity— *i*-amyl alcohol concentration curves of SAW-system (○) and AW-system (×) respectively. It is indicated in Fig. 5 that there are no differences perceptible in magnitude of viscosity coefficients between aqueous *i*-amyl alcohol solutions with and without saponin. In Fig. 4, on the other hand, we notice that the addition of saponin causes a marked increase in density of dilute

(10) Dunken, Fredenhangen and Wolf, *Kolloid-Z.*, **95**(1941), 186.

aqueous *i*-amyl alcohol, but the effect becomes less pronounced with increasing concentration and finally saponin decreases the density of the system in the region of sufficiently concentrated *i*-amyl alcohol solution (more than 0.18 mol. per liter). The value of the initial increase in density is far more than the calculated under the assumption of volumes additive for solute and solvent. These increase and subsequent decrease in density may perhaps be explained by a remarkable degree of solvation of saponin and its gradual change. The concentration of 0.18 mol. per litre may also be understood in connection with the strength of solvation. The details, however, are not yet certain.

Further it must be added that both viscosity and density change smoothly with *i*-amyl alcohol concentration, in which we cannot find any explanation sufficient to account for the peculiar nature in foam of SAW-system observed near C_0-point.

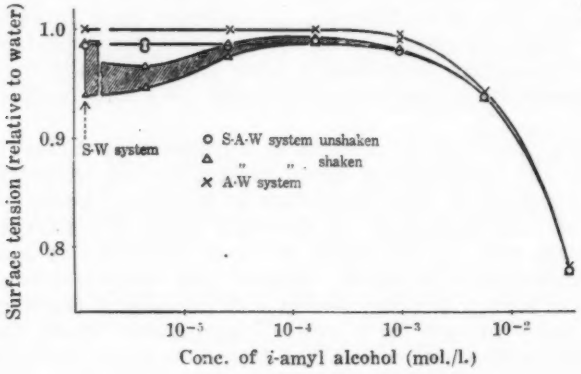

Fig. 6.

Fig. 6 indicates surface tension—*i*-amyl alcohol concentration curves of SAW- and AW- systems (circlet and cross marks respectively). Here we can also neither make distinction between the system with and without saponin, nor find any explanation for the above mentioned peculiarity in foam phenomena. More precise measurement on surface tension, mainly in dilute *i*-amyl alcohol concentration, however, revealed the following interesting but complicated phenomena.

Surface tension of SAW-system often shows change with time. The tension gradually increases with the age of fresh surface and finally reaches to a limiting constant value. The effect is usually more remarkable when we shake a solution shortly before the measurement. These circumstances were also recorded in Fig. 6, in which circlet and cross represent unshaken systems (mentioned above) and triangle, shaken ones. In latter systems, minimum surface tension values of relatively fresh surface and nearly maximum tension often attained after about ten or twenty minutes were recorded for each concentration of *i*-amyl alcohol. Hatching indicates the aging effect. Observed amounts of change in surface tension fluctuate considerably even for one and the same concentration, but as a whole, we can see in the figure that the

effect is most remarkable for the system without *i*-amyl alcohol, then it gradually diminishes with increasing concentration and finally disappears at sufficiently high concentration of the alcohol. These phenomena together with the fact that the surface tension of an aqueous *i*-amyl alcohol shows no effect of aging, again as in the case of foam properties, led us to the conclusion that the surface layer of SAW-system changes from simple solution of saponin, through mixed solution of saponin and *i*-amyl alcohol, again to simple solution of *i*-amyl alcohol with increasing concentration of the alcohol. The transition of these surface properties occurs in the region of alcohol concentration of from 10^{-5} to 10^{-2} mol. per litre, which roughly coincides with the case of foam properties.

In connection with surface aging of solutions one question at least is still left unanswered, viz., what is the cause of the phenomena of aging. Such a problem or more generally the questions of surface aging of colloidal solutions have been treated by a number of workers[11] and the present authors also have intension to continue their investigations on these lines. Here, we merely point out that such aging phenomena often appear in SAW-system immediately after shaking, while they disapper when we prepare the system without shaking. We need further investigations.

Regarding the foam phenomena as a measure of surface properties, we can trace the behaviour of liquid surface by the observation of the change in magnitude of foam formation as mentioned above. As for the mechanism of foam formation, on the other hand, it is another problem. In SAW-system near C_0 the degree of foam formation as has been was described, enormously increases without any measurable changes or singularities in surface tension, density and viscosity of the system. Thus at least we failed to seek for a simple explanation. These are sufficient to suggest the existence of some other factors or ideas which must be introduced to explain the mechanism of foam formation. In the previous and present reports, we adopted the conception of foam producing power and foam stability,[8] but they are rather conventional ones which require further explanations based on more fundamental physico-chemical properties well defined.

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(11) du Noüy, "Surface equilibria of colloids," New York (1926); Doss, *Kolloid-Z.*, **87**(1939), 272; Boutaric and Berthier, *Bull. Soc. Chim. France*, **6**(1939), 804; Hauser and Swearingen, *J. Phys. Chem.*, **45**(1941), 644; Alexander, *Trans. Faraday Soc.*, **37**(1941), 15; Mc Bain and others, *J. Am. Chem. Soc.*, **62**(1940), 1319; **63**(1941), 1422; Harkins and Nutting, *J. Am. Chem. Soc.*, **62**(1940), 1496; Nutting and Long, *J. Am. Chem. Soc.*, **63**(1941), 84.

Synthesis of Tertiary Butyl Alcohol by the Hydration of Isobutylene. IV. Some Attempts for the Confirmation of the Formation of Tertiary Butyl Sulphates, and Discussions on the Reaction Mechanism.

By Masaharu KATUNO.

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4·1. Some Attempts for the Confirmation of the Formation of *tert*-$C_4H_9OSO_3H$.

Although the formation of *tert*-$C_4H_9OSO_3H$ has been assumed as an intermediate product in the hydration and polymerisation of isobutylene with sulphuric acid[2], no indication has been observed of its formation in the previous report[3]. In case of the hydration of secondary olefines, such as propylene and *n*-butylene, the formations of *sec*-$ROSO_3H$ and $(sec\text{-}R)_2SO_4$ were distinctly confirmed[4], and *sec*-$ROSO_3H$ became very stable by conversion into sodium salt or *sec*-$ROSO_3^-$ ion. In the present investigation some experiments were made for the purpose of the comfirming *tert*-$C_4H_9OSO_3H$ as sodium and barium salts, but no indication of the ester formation was observed.

Since there is the possibility of the decomposition of *tert*-$C_4H_9OSO_3Na$ into *tert*-butanol in the course of the distillation of the alkaline solution, obtained by the neutralization of the absorption product of isobutylene with sulphuric acid, the solution has been extracted at room temperature to remove the free *tert*-butanol completely, and the remaining solution has then been distilled to obtained *tert*-butanol, which is expected to be produced from *tert*-$C_4H_9OSO_3Na$. However, little *tert*-butanol has been obtained by the distillation of the remaining solution, showing that *tert*-butanol corresponding to the amount of isobutylene absorbed had been completely extracted with ether.

The absorption product of isobutylene with 67% sulphric acid was diluted and neutralised by the addition of sodium hydroxide solution with vigorous stirring below 20°C. (DE 309), or it was dropped into excess sodium hydrooxide solution vigorously stirred below 10°C. (DB 308), with the same negative results.

B. T. Brooks and I. Humphrey[5] reported that they obtained barium salts of acidic sulphates of tertiary alcohols, such as *tert*-$C_6H_{13}OSO_3\frac{Ba}{2}$

(1) This paper is the 9th report on the hydration of olefines into alcohols; Previous Paper: this Bulletin, **18**(1943), 251.

(2) cf. M. Katuno, *J. Soc. Chem. Ind., Japan*, **44**(1941), 392B, 363B, **45**(1942), 211B.

(3) M. Katuno, *ibid.*, **44**(1941), 392B.

(4) cf. M. Katuno, *ibid.*, **43**(1940), 8B, 11B, **44**(1941) 275B, 279B.

(5) B. T. Brooks and I. Humphrey, *J. Am. Chem. Soc.*, **40**(1918), 822.

and *tert*-$C_7H_{15}OSO_3\frac{Ba}{2}$, by treating tetramethyl ethylene and γ-ethyl-β-pentene with sulphuric acid. In the present investigation the separation of barium salt of *tert*-$C_4H_9OSO_3H$ has been attempted, though with negative results.

The absorption product of isobutylene with 67% sulphuric acid below 20°C. was diluted and neutralised by the addition of $Ba(OH)_2 \cdot 8H_2O$, or it was dropped into the aqueous suspension of excess $Ba(OH)_2 \cdot 8H_2O$, vigorously stirred. After removing an excess of barium hydroxide by filtration and by precipitation with saturation of carbon dioxide followed by filtration of barium carbonate, the filtrate was evaporated in a bath under reduced pressure at 45°C. A small amount of barium salt corresponding to the formula $C_4H_9OSO_3\frac{Ba}{2}$ was obtained. It was very stable and the decomposition of its acidic solution yielded not *tert*-butanol, but *sec*-butanol, showing that the salt obtained was *sec*-$C_4H_9OSO_3\frac{Ba}{2}$ which, probably, had been produced from normal butylene contained as impurity in isobutylene gas. Thus *tert*-$C_4H_9OSO_3H$ has not been confirmed in the present investigation.

It is also doubtful that the barium salts obtained by Brooks and Humphrey contain tertiary radicals, because there is the possibility of the rearrangement of tertiary alkyl radical into secondary, such as

$$(CH_3)_2CH-\underset{\displaystyle OH}{\underset{|}{C}}(CH_3)_2 \longrightarrow (CH_3)_3C\cdot\underset{\displaystyle OH}{\underset{|}{C}}H\cdot CH_3\ ,^{(6)}$$

and of the existence of secondary isomeric olefines contained as impurities.

Experimental Details. 1. *Experiment for the Confirmation of* *tert*-$C_4H_9OSO_3Na$, *No. 1.* (DB 309). 76.5 g. (1.365 mol.) of isobutylene was absorbed with 143 g. of 67% sulphuric acid with vigorous stirring at 15–17°C. for $4\frac{15}{60}$ hrs. The product was diluted with 190 g. of water with vigorous stirring below 20°C., and then made strongly alkaline to phenolphthalein with concentrated sodium hydroxide solution below 20°C.

tert-Butanol separated was removed and the aqueous layer was extracted five times with each 100 c.c. of ether, after dissolving sodium sulphate by adding water and warming slightly. The aqueous solution obtained was distilled through a 30 cm. Widmer column to obtain a distillation curve against the weight of the distillate. The boiling point rised rapidly to that of water, after a small amount of ether dissolved, had been distilled away, but little *tert*-butanol-water azeotropic mixture (b.p. 79.9°C) was observed.

2. *Experiment for the Confirmation of* *tert*-$C_4H_9OSO_3Na$, *No. 2.* (DB 308). 72.5 g. (1.295 mol.) of isobutylene was absorbed with 143 g. of 67% sulphuric acid with vigorous stirring for $6\frac{20}{60}$ hrs. at 15–18°C. The product was dropped into 20% sodium hydroxide solution (450 g.)

(6) K. C. Laughlin, C. W. Nash and F. C. Whitmore, *J. Am. Chem. Soc.*, **56** (1934), 1395; F. C. Whitmore and P. L. Meunier, *ibid.*, **63** (1941), 2197.

which was stirred vigorously and cooled below 10°C. Water was added, if necessary, in the course of the neutralisation. The product was diluted with water to about 1 l. and slightly warmed to dissolve sodium sulphate completely. Then it was extracted five times with each 100 c.c. ether. The aqueous solution, separated from free *tert*-butanol was refluxed for 2 hrs, and then distilled, using a 30 cm. Widmer column, to draw a distillation curve. The boiling point rised rapidly to that of water after distilling a small amount of ether, but *tert*-butanol-water azeotropic mixture was hardly observed.

3. *The Experiment to separate tert*-$C_4H_9 \cdot OSO_3\frac{Ba}{2}$, *No. 1.* (DB 301). 51.2 g. (0.915 mol.) of isobutylene was absorbed with 143 g. of 67% sulphuric acid for $4\frac{49}{60}$ hrs. with vigorous stirring at 18–21°C. The product was diluted with 200 c.c. of water below 20°C. with stirring and 400 g. (1.27 mol.) of the powder of $Ba(OH)_2 \cdot 8H_2O$ was added little by little with vigorous stirring below 20°C., water being added when necessary. The product was filtered from barium sulphate and excess $Ba(OH)_2 \cdot 8H_2O$, and saturated with CO_2, then filtered from barium carbonate. The filtrate was evaporated in a thermostat under reduced pressure at 45°C. and about 3.4 g. of white solid was obtained.

4. *The Experiment for the Separation of* tert-$C_4H_9OSO_3\frac{Ba}{2}$, *No. 2.* (DB 303). 53 g. (0.95 mol.) of isobutylene was absorbed with 143 g. of 67% sulphuric acid for $6\frac{15}{60}$ hrs. at 14–18°C. The product was dropped into the mixture of 300 c.c. water and 377 g. (1.2 mol.) of the powder of $Ba(OH)_2 \cdot 8H_2O$, stirred vigorously and cooled below 10°C. The product showed alkaline to phenolphthalein.

The product was filtered, and the filtrate was saturated with carbon dioxide to precipitate barium carbonate, which was then filtered. The filtrate was evaporated in the thermostat under reduced pressure at 45°C, and 4.6 g. of white crystalline solid was obtained.

The white solid obtained in both of the experiments is soluble in water, and precipitates barium sulphate by the addition of sulphuric acid. On boiling its aqueous solution, however, it is stable and does not precipitate barium sulphate by the decomposition.

Anal. C: 20.21%, 20.20%; H: 4.33%, 4.32%; Ba: 28.24%, 28.39%.

Calcd. for $C_4H_9OSO_3\frac{Ba}{2}$: C: 21.65%; H: 4.09%; Ba 30.96%.

5. *The Isolation of sec*-C_4H_9OH *from the* $C_4H_9OSO_3\frac{Ba}{2}$. 2.7 g. of the $C_4H_9OSO_3\frac{Ba}{2}$ obtained was dissolved in 3.5 c.c. of water, and was then mixed with 42 g. of 60% sulphuric acid, when barium sulphate precipitated. After being kept on standing 3 hrs., 33 c.c. of water was added below 20°C. and then made strongly alkaline with 120 g. of 20% sodium hydroxide solution. Phenolphthalein was not added to avoid the contaminating by ethyl alcohol. The product was then distilled with a 20 cm. Widmer column and 8.8 g. of distillate boiling at 97–99°C was obtained (Distillate A). The residue was then distilled after acidifying with 100 g.

of 50% sulphuric acid[7], and 10.5 g. of distillate boiling at 98–99°C. was obtained (Distillate B). The reactions of both distillates and those of *sec*- and *tert*- butanol are as follows.

	Distillate A	Distillate B	*sec*-C_4H_9OH	*tert*-C_4H_9OH
Iodoform reaction	Faint	Positive	Positive	Negative
Reaction against conc. HCl	Transparent	Transparent	Transparent	Turbulent
Reaction against Nessler reagent ...	Weak	Orange ppt.	Orange ppt.	Faint ppt.

Thus the distillates showed not the reactions of *tert*-butanol, but those of *sec*-butanol. The concentration of *sec*-butanol is small in the distillate A. The barium salt obtained is, therefore, *sec*-$C_4H_9OSO_3\overset{Ba}{}_2$, derived from normal butylenes probably contained as impurities in the isobutylene gas.

4·2. Discussion on the Reaction Mechanism of Hydration of Isobutylene.

The hydration of isobutylene, which belongs to the tertiary olefine, is markedly different from that of secondary olefines, such as, propylene and *n*-butylenes. Namely, (1) isobutylene can be absorbed rapidly with more dilute sulphuric acid, and it is polymerised more readily than secondary olefines, as is well known. (2) *tert*-Butanol formed in the acid phase can be extracted completely from the absorption product of isobutylene with sulphuric acid after being diluted with water, while in case of secondary olefines[8] a considerable amount of secondary alcohol remains unextracted in the form of stable acidic sulphate. (3) *tert*-Butanol can be completely recovered by distillation or by extraction from the absorption product of isobutylene with sulphuric acid, after being neutralized with excess alkali, in contrast with the fact that, in case of secondary olefine, a considerable amount of alcohol exists in the form of the stable acidic sulphate salt, such as *sec*-$C_4H_9OSO_3Na$[9], which undergoes little hydrolysis. (4) No formation of di-*tert*-alkyl sulphate was observed even when isobutylene was absorbed with 67% sulphuric acid to saturation, while in case of secondary olefines, such as propylene and *n*-butylene, di-*sec*-alkyl sulphate was formed and easily separated[10]

The above differences can be readily explained by the analogous reaction mechanism as in the hydration of secondary olefines[11], only by assuming the rapid hydrolysis of sulphuric acid ester of *tert*-butanol, forming the following equilibrium state.

(7) M. Katuno, *J. Soc. Chem. Ind., Japan*, **44**(1941), 275B, Expt. DA25.
(8) B. T. Brooks, *Ind. Eng. Chem.*, **27**(1935) 282.
(9) M. Katuno, *J. Soc. Chem. Ind., Japan*, **44**(1941), 275B.
(10) B. T. Brooks, *Ind. Eng. Chem.*, **27**(1935), 282; M. Katuno, *J. Soc. Chem. Ind., Japan*, **43**(1940), 11B; **44**(1941), 275B.
(11) M. Katuno, *ibid.*, **43**(1940), 8B, 11B; **44**(1941), 275B.

$$i\text{-}C_4H_8 \underset{-H_2SO_4}{\overset{+H_2SO_4}{\rightleftharpoons}} t\text{-}C_4H_9\cdot OSO_3H \underset{-H_2O+H_2SO_4}{\overset{+H_2O-H_2SO_4}{\rightleftharpoons}} t\text{-}C_4H_9OH$$

There seems no necessity to assume other reaction mechanism, which differs essentially from that for the hydration of secondary olefines, for the hydration of tertiary olefine. Sulphuric acid is added to the double bond of isobutylene reversibly to form *tert*-$C_4H_9OSO_3H$, which is highly reactive and undergoes hydrolysis immediately to establish the above equilibrium. *tert*-$C_4H_9OSO_3H$ is an important intermediate compound not only in the hydration of isobutylene, but also in the polymerisation of isobutylene according to the most reliable mechanism of the type of Lwow[12].

The assumption of the high reactivity for *tert*-$C_4H_9OSO_3H$ is probable, judging from the following facts concerning the high reactivity of tertiary alkyl radicals. Namely, *tert*-butanol is converted immediately into *tert*-butyl chloride,[13] by mixing with concentrated hydrochloric acid, while the analogous reactions of primary and secondary alcohols are slow. Tertiary alkyl chlorides, in general, undergo more rapid hydrolysis than secondary and primary alkyl chlorides[14]. *Tert*-butyl acetate is more readily hydrolised than *sec*- and *prim*-alkyl acetates in neutral or acidic solution[15] although less readily in alkaline[16]. It reacts rapidly with hydrobromic acid[15a]. Ethers containing *tert*-alkyl radicals, including the recently known di-*tert*-butyl ether[17], undergo decomposition readily with acids.[18]

The fact that no indication of the formation of *tert*-butyl sulphate could be found in the present investigation may also be explained as follows. Namely, although *tert*-$C_4H_9OSO_3H$ may be formed in the equilibrium mixture, it is hydrolysed completely into *tert*-butanol, on the dilution and neutralisation with alkali, due to the rapid shift of the equilibrium. The fact that the same results are obtained even when the absorption product is dropped into the alkaline solution vigorously stirred, suggests that the hydrolysis of *tert*-$C_4H_9OSO_3H$ takes place very rapidly. The complete extraction of *tert*-butanol from the sulphuric acid solution can also be readily explained by the above equilibrium. It is not yet known whether *tert*-$C_4H_9OSO_3Na$ is stable like *sec*-$ROSO_3Na$ or not.

Although the formation of di-*tert*-butyl sulphate ((*tert*-$C_4H_9)_2SO_4$)

(12) M. Katuno, *ibid.*, **44**(1941), 363B; cf. Kondakow, J. Prakt. Chem., (2) **54**(1896), 442.

(13) "Organic Synthesis."

(14) E. E. Ayres, *Ind. Eng. Chem.*, **21**(1929), 899; H. M. Woodburn and F. C. Whitmore, *J. Am. Chem. Soc.*, **56**(1934), 1394.

(15) H. S. Davis and W. J. Murray, *Ind. Eng. Chem.*, **18**(1926), 844; A. Skrabal and A. M. Hugetz, Monatsh, **47**(1928), 17; M. H. Palomaa, *etal.*, *Ber.*, **68**(1935), 303; (15a) B. W. Tronow and N. C. Ssibgatulin, *Ber.*, **62**(1929), 2850.

(16) A. Skrabal and A. M. Hugetz, loc. cit.; W. M. D. Bryant and D. M. Smith, *J. Am. Chem. Soc.*, **58**(1936), 1014.

(17) J. L. E. Erickson and W. H. Ashton, *ibid.*, **63**(1941), 1769.

(18) J. F. Norris and G. Y. Rygby, *ibid.*, **54**(1932), 2088; T. W. Evans and K. R. Edlund, *Ind. Eng. Chem.*, **28**(1936), 1186.

was not observed, there would be the possibility of its formation according to the following equilibrium,

$$t\text{-}C_4H_9\cdot OSO_3H + t\text{-}C_4H_9OH \rightleftarrows (t\text{-}C_4H_9)_2SO_4 + H_2O$$

or $$2\,t\text{-}C_4H_9\cdot OSO_3H \rightleftarrows (t\text{-}C_4H_9)_2SO_4 + H_2SO_4$$

and it may disappear immediately due to the shift of equilibrium, on dilution or neutralisation.

Isobutylene can be slowly absorbed with dilute acid of less than 1 N concentration[19]. H. J. Lucas and W. F. Eberz[19] used the following hydration mechanism including hydrogen ion.

$$i\text{-}C_4H_8 + H_3O^+ \longrightarrow t\text{-}C_4H_9OH + H^+$$

However, the rapid absorption of isobutylene with concentrated acid, such as 67% in weight shows that the reaction with undissociated sulphuric acid, as shown by the mechanism described above, takes place rapidly.

4·3. Summary.

1. The confirmation of *tert*-$C_4H_9OSO_3H$, which has been assumed as the intermediate compound in the hydration and polymerisation of isobutylene with sulphuric acid, has been attempted in the form of sodium or barium salts though with negative results.

2. The reaction mechanism of the hydration reaction of isobutylene with sulphuric acid has been discussed. Experimental results can be explained by the assumption that *tert*-$C_4H_9OSO_3H$ formed is very reactive to undergo rapid hydrolysis to establish the following equilibrium rapidly.

$$i\text{-}C_4H_8 \underset{-H_2SO_4}{\overset{+H_2SO_4}{\rightleftarrows}} t\text{-}C_4H_9\cdot OSO_3H \underset{-H_2O+H_2SO_4}{\overset{+H_2O-H_2SO_4}{\rightleftarrows}} t\text{-}C_4H_9OH$$

The author wishes to express his thanks to Mr. Y. Ban and Mr. M. Kurokawa for their guidance, to Mr. S. Nagaoka and Y. Oonogi for their assistance in the experiments and to the analytical department of this institute for the elementary analysis.

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(19) H. J. Lucas and W. F. Eberz, *J. Am. Chem. Soc.*, **56**(1934), 460; H. J. Lucas and Y. P. Lin, *ibid.*, **56**(1934), 2138.

On the Hydrogenation and Polymerisation Reaction of Acetylene. IV.[1],[2] Kinetics of Polymerisation by Use of Thermal Separation Column. II.

By Osamu KIMURA and Kozo HIROTA.

(Received March 30, 1943.)

It has been found by the authors[1] that the thermal separation column of Clusius and Dickel can be applied to the polymerisation of acetylene very effectively. As described in the previous paper, it was also shown[2] that the apparatus could be used for the study of kinetics of the concerned reaction, because the velocity of the reaction could be followed more distinctly than by the usual method, so that the order of the reaction was clearly determined to be of the second order. However, as there existed temperature gradient in the reaction vessel, the true reaction velocity constant or the velocity constant at any definite temperature could not be evaluated directly. Consequently the activation energy obtained according to the Arrhenius' equation contained some ambiguity, though it was not much different from the value determined by H. A. Taylor and van Hook[3] by the usual static method. The reason for this coincidence may be due to the fact that the reaction velocity increases rapidly as the temperature rises, and that the reaction takes place practically in the vicinity of the filament. In spite of the above coincidence the value thus obtained remains to be of preliminary nature, so the following method is devised to obtain the true velocity constant and the true activation energy.

Calculation of the Velocity Constant. It is considered that the amount of reaction in unit time at any elementary space in the reaction vessel is given by the kinetic mass action law. The total amount of the reaction in the same time is, therefore, obtained by the integrated amount in the whole reaction space. As determined in the previous paper, the concerned reaction is of the second order, the reaction velocity is given by the following equation:

$$\frac{dn}{dt} = \int_{r_1}^{r_2} k_c \cdot C^2 \cdot l 2\pi r \cdot dr \qquad (1)$$

where k_c is the velocity constant at concentration C, l is the length of the filament, r_1 and r_2 are the radii of the filament and the reaction vessel, and r is the radial distance measured from the center axis of the reaction vessel. In the above equation, it is convenient to replace C by P which is constant at everywhere in the apparatus. Between these quantities there exists a relation,

(1) The second report, this Bulletin, 18(1943), 13.
(2) The third report, *ibid.*, 18(1943), 45.
(3) H. A. Taylor and A. van Hook, *J. Phys. Chem.*, 39(1935), 811.

$$C = P/RT\,. \tag{2}$$

Then, according to the Arrhenius' equation, putting k_c as

$$k_c = A_c e^{-\frac{Q}{RT}}\,, \tag{3}$$

we obtain from equations (1), (2), and (3),

$$\frac{dn}{dt} = \frac{2\pi l P^2 A_c}{R^2}\int_{r_1}^{r_2}\frac{e^{-\frac{Q}{RT}}}{T^2}\cdot r dr\,. \tag{4}$$

If we designate the volume of the reaction vessel by V_0 and the room temperature by T_0

$$\frac{dn}{dt} = V_0\frac{dc}{dt} = \frac{V_0}{RT_0}\frac{dp}{dt}\,. \tag{5}$$

Therefore,

$$\frac{dP}{dt} = P^2\frac{2\pi l A_c T_0}{RV_0}\int_{r_1}^{r_2}\frac{e^{-\frac{Q}{RT}}}{T^2}\cdot r dr\,. \tag{6}$$

By definition,

$$\frac{dP}{dt} = k_p P^2\,, \tag{7}$$

so

$$k_p = \frac{2\pi l A_c T_0}{RV_0}\int_{r_1}^{r_2}\frac{e^{-\frac{Q}{RT}}}{T^2}\cdot r dr\,. \tag{8}$$

To calculate the value of k_p, we must know the relation between T and r, i.e., the distribution function of the temperature in the reaction vessel. As the length of the column is much larger than its diameter, it may be allowed to neglect the longitudinal flow of heat, provided that the system is in stationary state. Moreover, the temperature rise due to the absorption of radiant energy from the filament can be neglected in our case. Then the temperature distribution can be given by the following differential equation:

$$\frac{d^2T}{dr^2} + \frac{1}{r}\frac{dT}{dr} = 0 \tag{9}$$

The general solution of this equation is

$$T = C_1 \log r + C_2\,, \tag{10}$$

where C_1 and C_2 are the integration constants. Taking into account of the boundary conditions that the temperatures of the filament and the outer wall are kept constant: T_1 and T_2, the temperature at the distance r will be given by

$$T = \frac{(T_2-T_1)\log r + T_1 \log r_2 - T_2 \log r_1}{\log r_2 - \log r_1} . \qquad (10')$$

From equation (8) and (10'), the value of k_p will be obtained at once provided that the integration is possible, but as it is not, the following approximate method is adopted.

Considering that $r_2 \gg r_1$, r_1 is taken as the unit of length, so $\log r_1 = 0$. Then equation (10') will be simplified as

$$T = \frac{(T_2-T_1)\log r + T_1 \log r_2}{\log r_2} \qquad (11)$$

or

$$\frac{1}{T} \fallingdotseq \frac{1}{T_1}\left\{1 - \frac{T_2-T_1}{T_1}\frac{\log r}{\log r_2}\right\} . \qquad (12)$$

Taking into consideration that $e^{-\frac{Q}{RT}} \gg 1$, when r is comparable with r_2, the integrand of equation (8) becomes(*)

$$\int_{r_1}^{r_2} \frac{e^{-\frac{Q}{RT}}}{T^2} r dr \fallingdotseq \frac{r_1^2}{T_1^2}\int_{r_1}^{r_2} r\, e^{-\frac{Q}{RT}\left(1+\frac{\Delta T}{T_1}\frac{\log r}{\log r_2}\right)}\left(1+\frac{2\Delta T}{T}\frac{\log r}{\log r_2}\right)dr ,$$

where $\Delta T = T_1 - T_2$. By partial integration it becomes

$$r_1^2 e^{-\frac{Q}{RT}} (I_1 + I_2)/T_1^2 , \qquad (14)$$

where

$$I_1 = 1\Big/\left(\frac{Q}{RT_1^2}\frac{\Delta T}{\log r_2} - 2\right) + \frac{2\Delta T}{T_1 \log r_2}\Big/\left(\frac{Q}{RT_1^2}\frac{\Delta T}{\log r_2} - 2\right)^2 ,$$

$$I_2 = \left\{\left(1+\frac{2\Delta T}{T_1}\right)\Big/\left(2 - \frac{Q}{RT_1^2}\frac{\Delta T}{\log r_2}\right) - \frac{2\Delta T}{T_1 \log r_2}\Big/\left(\frac{Q}{RT_1^2}\frac{\Delta T}{\log r_2} - 2\right)^2\right\} r_1^2 e^{-\frac{Q}{RT_1^2}\Delta T} ,$$

Then

$$k_p = r_1^2 \frac{2\pi l A_c T_0}{VR} \frac{e^{-\frac{Q}{RT}}}{T_1^2}(I_1 + I_2) , \qquad (15)$$

or taking the logarithm

$$\log_{10} k_p = \log_{10} \frac{2\pi l A_c T_0}{VR} r_1^2 - \frac{Q}{RT}\log_{10} e - 2\log_{10} T_1 + \log_{10}(I_1 + I_2) .$$

The last formula has two unknown constants, A_c and Q. We can therefore determine them, if two or more measurements of k_p are done provided that the evaluation can be done numerically.

(*) Factor r_1^2 before the integrand occurred, because r_1 was taken as the unit of radial length.

Velocity Constant and Heat of Activation of the Polymerisation of Acetylene. According to the method described above, the velocity constant and the heat of activation of the concerned reaction is carried out. The experimental data used in the calculation are described in Table 1.

Table 1. Velocity of Polymerisation of Acetylene.[2]

Dimension of the reaction tube (thermal separation tube).

Outer radius of the filament ($2r_1$)	0.1 mm.
Length of the filament (l)	51 cm.
Inner diameter of the tube ($2r_2$)	1.5 cm.
Length of the tube	100 cm.
Volume of the tube	305 c.c.

Temp. of the filament (°C.)	Apparent velocity constant k_p (cm. Hg^{-1}, $min.^{-1}$)
720	0.000082
805	0.00042
850	0.0011
895	0.0021

The result of the calculation is as follows:

$$Q = 44\,\text{kcal.}, \qquad A_c = 3.0 \times 10^{15}\ \text{(c. g. s.)}$$

The activation energy is found to be slightly smaller than the preliminary value of the previous paper (44.8 kcal.), but larger than that given by Taylor and van Hook (40.5 kcal. and 42 kcal. at 495° and 595°C., respectively). On the other hand, the values of k_p at 720° and 500°C. are calculated by equation (3), and shown in Table 2 together with those of other authors. It is shown that our values are considerably larger than those given by Pease[4] and by Taylor and van Hook[3]. However, considering that Taylor was obliged to assume the product as tetramer arbitrarily in order to obtain the above values, and that the temperature interval of the measurement is different, the agreement will be satisfactory.

Table 2. Velocity Constants of Polymerisation of Acetylene by Various Authors.

Temp. (°C.)	k_p (Atm.$^{-1}$, sec.$^{-1}$)	Authors
420	0.005–8	Schläpfer and Brunner
450	0.00016–22	Pease
495	0.0039	Taylor and van Hook
500	0.0011–15	Pease
"	0.020	Kimura and Hirota (extrapolated value)
515	0.0078	Taylor and van Hook
535	0.0145	" " "
550	0.0049–11	Pease
600	0.025–45	"
720	8.7	Kimura and Hirota.

(4) R. N. Pease, *J. Am. Chem. Soc.*, **51** (1929), 3470.

Summary.

(1) A method for calculating both reaction velocity and activation energy in the case when the reaction has been carried out in the thermal separation column of Clusius and Dickel has been described.

(2) The method has been applied to the polymerisation reaction of acetylene previously investigated by the present authors.

(3) It has been found that the calculated heat of activation is slightly smaller than our preliminary value, but larger than the directly observed value by Taylor and van Hook, and that the calculated velocity constants are several times larger than those hitherto have been observed.

In conclusion, the authors express their sincere thanks to Dr. M. Sato, the Director of the Laboratory, and also to Dr. R. Yoshimura, the Chief of the Department of Inorganic Chemistry, for their encouragement throughout this research.

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On the Dispersion of the Hydroxides of Manganese, Iron, Cobalt and of Copper by Autoclaving in the Presence of Aluminium Hydroxide.

By Tominosuke KATSURAI.

(Received June 28, 1943.)

When aluminium hydroxide is subjected to autoclaving, it undergoes imbibition and turns out to be a very stable sol[1]. On the contrary, it is well known that ferric hydroxide undergoes dehydration by autoclaving, and turns out to be a compact mass of crystalline structure. If we subject the mixture of these two hydroxides to autoclaving and observe the competition of the two opposing tendencies, i.e., imbibing tendency and dehydrating tendency, we see that the imbibing tendency of aluminium hydroxide predominates and that a rather stable sol is obtained, which contains hydroxides both of aluminium and iron[2].

It is thought that such dispersion might be expected for the hydroxide of other metal, which itself shows dehydrating tendency under autoclaving. Performing the experiment as in the case of Al~Fe hydroxides,

(1) T. Katsurai and T. Kita, *Bull. Chem. Soc. Japan*, **15**(1940), 458; *Kolloid-Z.*, **95**(1941), 41.

(2) T. Katsurai and T. Kita, *Sci. Pap. Inst. Phys. Chem. Research* (Tokyo), **40**(1942), 70.

some new sols are obtained. In the following, the results are given in each case.

1. Autoclaving of the Hydroxides of Mn, Co, Ni, Cu and of Pb.

The hydroxides are precipitated by adding sodium hydroxide, in a slight excess, to the chlorides of manganese, cobalt, nickel and of copper, and ammonia to the nitrate of lead. In each case, decantation and washing are repeated until the supernatant liquid gives no colouration with phenolphthalein. The hydroxide and the supernatant liquid are then shaken together, and the resulting temporary suspension is removed to a vessel of fused quartz. The vessel is placed in an autoclave of steel and is heated up to 190°C. and is kept one hour at this temperature[3].

By this treatment the hydroxides of manganese, cobalt, and of copper turn out to compact precipitates which settle on the bottom. Their colour is darker than that of the hydroxides which are put to stand at the room temperature. The filtrates obtained by filtering the precipitates are clear and neutral and show no reaction of the metal.

The appearance of the Ni-hydroxide remains unchanged by this treatment. However, the hydroxide can be completely filtered, giving a clear, neutral solution containing no nickel.

The Pb-hydroxide coagulates and settles by this treatment. The supernatant liquid is clear. The precipitate can be filtered, giving a clear, neutral filtrate containing no lead.

Thus by these experiments, we see that the hydroxides show more or less dehydrating tendency.

2. Autoclaving of the Hydroxides of Mn, Fe, Co, Ni, Cu and of Pb in the Presence of Aluminium Hydroxide.

The aluminium hydroxide is precipitated by adding ammonia, in a slight excess, to aluminium chloride. Washing and decantation are repeated until the supernatant liquid shows no colouration with phenolphthalein. The hydroxide is then mixed with each of the hydroxides of manganese, cobalt, nickel, copper and lead (except iron), and is subjected to the 190°–1 hr. treatment. In each experiment the content of the quartz vessel is filtered and the colloidal behaviour of the filtrate is observed.

a. *Al~Mn hydroxides*: As starting materials, 4 g. of aluminium chloride ($AlCl_3 \cdot 6H_2O$) and 3 g. of manganese chloride ($MnCl_2 \cdot 4H_2O$) are used. By autoclaving, a dark brown suspension with some deposit is obtained. The filtrate is a stable sol. By chemical analysis, its composition is found to be

$$Al_2O_3 = 2.00 \text{ mg./c.c.}, \qquad MnO_2 = 0.79 \text{ mg./c.c.},$$
$$Al_2O_3 : MnO_2 = 1 : 0.45 \text{ (mol. ratio)}.$$

b. *Al~Fe hydroxides*: The hydroxides are co-precipitated by adding ammonia to the solution obtained by dissolving 4 g. each of aluminium chloride ($AlCl_3 \cdot 6H_2O$) and ferric chloride ($FeCl_3 \cdot 6H_2O$) together. The

(3) For the details of the experimental technique, cf. T. Katsurai, *Sci. Pap. Inst. Phys. Chem. Research* (Tokyo), **35**(1939), 191.

remaining procedure is the same as in the other cases. A sol having the following composition is obtained[4].

$$Al_2O_3 = 0.93 \text{ mg./c.c.}, \qquad Fe_2O_3 = 1.08 \text{ mg./c.c.},$$
$$Al_2O_3 : Fe_2O_3 = 1 : 0.75.$$

c. *Al~Co hydroxides*: As starting materials, 4 g. of aluminium chloride ($AlCl_3 \cdot 6H_2O$) and 3 g. of cobalt chloride ($CoCl_2 \cdot 6H_2O$) are used. Dark blue sol having the following composition is obtained.

$$Al_2O_3 = 1.55 \text{ mg./c.c.}, \qquad CoO = 1.91 \text{ mg./c.c.},$$
$$Al_2O_3 : CoO = 1 : 1.67.$$

When this sol is shaken, it shows beautiful "schlieren effect".

d. *Al~Ni hydroxides*: No dispersion takes place by the autoclaving. The filtrate is clear and contains neither aluminium nor nickel.

e. *Al~Cu hydroxides*: 4 g. of aluminium chloride ($AlCl_3 \cdot 6H_2O$) and 2.5 g. of cupric chloride ($CuCl_2 \cdot 2H_2O$) are used for the preparation. Dark brown sol having the following composition is obtained.

$$Al_2O_3 = 3.78 \text{ mg./c.c.}, \qquad CuO = 3.88 \text{ mg./c.c.},$$
$$Al_2O_3 : CuO = 1 : 1.31.$$

This sol also shows "schlieren effect" when it is shaken[5].

f. *Al~Pb hydroxides*: No dispersion takes place by the autoclaving. The filtrate is clear and contains neither aluminium nor lead.

Summary.

The hydroxides of manganese, iron cobalt, nickel, copper and lead show, by autoclaving, more or less dehydrating tendency and undergo contraction of sedimentation volume.

The hydroxides of manganese, iron, cobalt and copper are dispersed by autoclaving in the presence of Al-hydroxide. The sols of the hydroxides of *Al~Co* and of *Al~Cu* show "schlieren effect".

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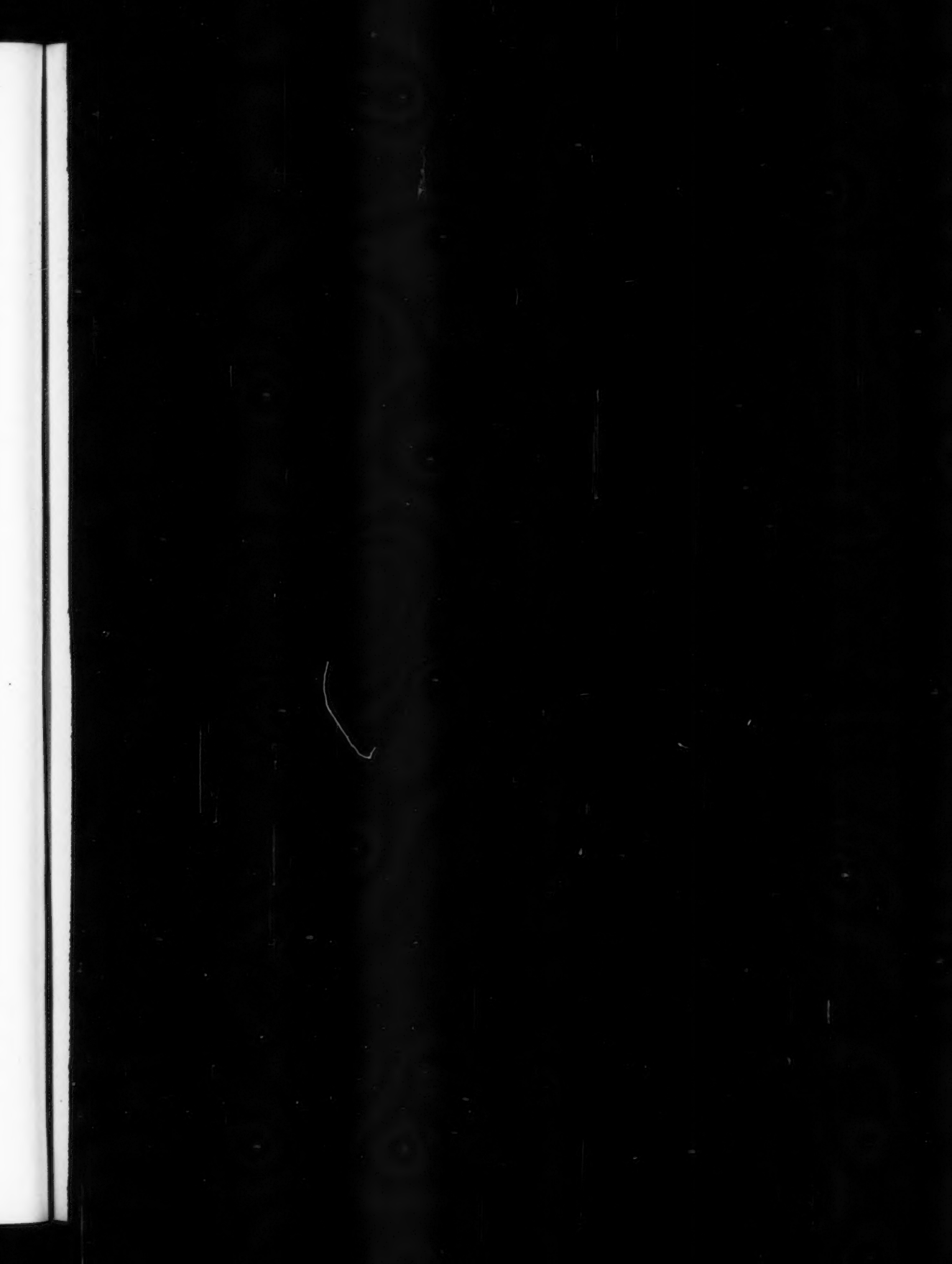
(4) It was stated in a previous paper that in order to disperse the Al–Fe hydroxides, it was necessary to precipitate the hydroxides of aluminium and iron separately. Cf. (2) p. 70 below. It was, however, found lately that the co-precipitated Al–Fe hydroxides can also be dispersed, when they are fresh, viz., not older than a day after precipitation. In the series of the present investigation, all the hydroxides are subjected to autoclaving within a day after precipitation.

(5) I should like to express my sincere thanks to Mr. K. Kuroda for carrying out the analysis of the sols.